PB84-209659

Tar Sands Leachate Study

(U.S.) Industrial Environmental Research Lab.-
Cincinnati, OH

Jun 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-209659

EPA-600/2-84-113
June 1984

TAR SANDS LEACHATE STUDY

by

Douglas W. Grosse

and

Linda McGowan

Oil Shale Energy Mining Branch
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-84-113		PB84 209659

4. TITLE AND SUBTITLE	5. REPORT DATE
Tar Sands Leachate Study	June 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Douglas W. Grosse Linda McGowan	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Industrial Environmental Research Laboratory U. S. Environmental Protection Agency Cincinnati, Ohio 45268	N104 Multimedia Energy
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Industrial Environmental Research Laboratory U. S. Environmental Protection Agency Cincinnati, Ohio 45268	Final Report
	14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

An inhouse research project was conducted by the EPA's Industrial Environmental Research Laboratory (IERL) at the T&E Facility in Cincinnati, Ohio, to provide information concerning the potential for release of contaminants to groundwater from in-situ and above-ground processed tar sands. This study examined the composition of the leachate that may be generated from raw tar sand cores and spent tar sand waste. In all, twelve different water quality tests plus trace metal analyses were conducted on the leachate samples generated from the shake and extraction procedures.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Tar Sands Leachate In situ combustion Tars Bituminous Oil Sands	Utah Wastewater Asphaltic Rocks Synthetic Fuels	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	38
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The material presented in this report has been collected from an in-house research project conducted as an initial effort to establish baseline data from which later environmental assessment can be made and related pollution control methods be developed. This information will also pinpoint research gaps so that priorities for subsequent efforts in this area be defined. Further information can be obtained from the Industrial Environmental Research Laboratory.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

TAR SANDS LEACHATE STUDY

ABSTRACT

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has conducted research to assess the potential for release of contaminants to ground and surface waters from in-situ and above-ground processing of western tar sands. The purpose of this effort is to provide information that will (1) assist Federal and State regulatory offices in permitting activities, (2) provide the EPA with a data base for reviewing monitoring plans submitted by developers of the tar sands industry and (3) support efforts by the Office of Solid Waste (OSW) in establishing guidelines for the ultimate disposal of solid wastes from tar sands operations. Such information will assist the development of an environmentally acceptable tar sands industry.

CONTENTS

Forward iii
Abstract iv
Figures vi
Tables vii

1. Introduction 1
   Asphalt Ridge 1
   Characterization 4
   Recovery of Bitumen 7
2. Research Protocol 8
   Experimental Program 8
   Materials and Methods 8
      Tar Sand Cores 8
      EP Toxicity Test 8
      ASTM (D-3987) Method 10
   Chemical Analysis 12
   Precision and Accuracy 12
3. Results 13
4. Discussion 26
5. Conclusions 28

References 29

FIGURES

Number		Page
1	Location map of major oil-impregnated rock deposits of Utah	2
2	Geological stratigraphy of Asphalt Ridge	3
3	General geology and oil-impregnated sandstones of Asphalt Ridge and Asphalt Ridge Northwest, Northeastern Uinta Basin, Utah	5
4	Sieve analysis of spent tar sands	9
5	Total suspended solids	14
6	Total organic carbon	15
7	Sulfate	16
8	Alkalinity as $CaCO_3$	17

TABLES

Number		Page
1	Measurement of Asphalt Ridge	4
2	Typical Tar Sands Composition (Uinta Basin)	4
3	Physical Property Analysis of Asphalt Ridge Tar Sands Bitumens	6
4	Laboratory Analyses for Tar Sands Samples	11
5	Sulfates	18
6	Chlorides	19
7	Fluorides	20
8	Sulfides	20
9	Alkalinity as $CaCO_3$	21
10	Conductivity	22
11	Total Suspended Solids	23
12	Total Organic Carbon Analysis	24
13	Trace Metal Analysis	25
14	Water Quality Standards	26
15	Water Quality Criteria for Priority Pollutants	27

SECTION 1

INTRODUCTION

Oil impregnated sandstone, commonly referred to as tar sands, constitutes the largest known non-fluid petroleum reserve in North America. The largest known deposit is the Athabasca deposit located in Alberta, Canada. The first commercial plant, operated by Great Canadian Oil Sands, Ltd. (GCOS) was built to produce a synthetic crude oil. Approximately 20 million barrels of synthetic crude oil, extracted from tar sands bitumen, are produced per year. Currently a number of companies and research groups in the United States are working on processes to recover bitumen from tar sands. The potential for commercialization of tar sands resources is great, particularly in Utah where approximately 90-95% of the known tar sands deposits in the United States are located.(1)

Preliminary studies on assessing the environmental implication of in-situ extraction, as well as above-ground retorting, are scarce. There is heightened concern in states such as Utah regarding the environmental impact on local water supplies from tar sands mining and in-situ recovery operations. Water plays an important role in the recovery of tar sands bitumen. The extent of the pollution problem associated with the water usage has not been thoroughly examined.

An in-house research project was conducted by the EPA's Industrial Environmental Research Laboratory (IERL) at the Test and Evaluation (T&E) Facility in Cincinnati, Ohio, to provide information concerning the potential for release of contaminants to groundwater resources from in-situ and above-ground processing of tar sands. The experimenters conducting this study aim to examine the composition of the leachate that may be generated from raw tar sand cores and spent tar sands waste. The Resource Conservation Recovery Act's (RCRA) Extraction Procedure, (EP) Toxicity Test was used to simulate such a leachate generation.

Asphalt Ridge

Near surface deposits located in Utah are estimated to contain as much as 29 billion barrels of petroleum, as embedded bitumen in approximately 50 known groups of deposits in and near the Uinta Basin of northeastern Utah and in the southeastern portion of the state.(1) With regard to surface extraction operations, one of the more accessible major deposits in the United States is located at Asphalt Ridge near Vernal, Utah in the Uinta Basin (3) (see Figure 1). Tar sands deposits occur in a variety of stratigraphic and structural circumstances (see Figure 2).(3) The Uinta Basin grouping of deposits contain petroleum which probably originated in Eocene lacustrine source rocks of the Green River formation.

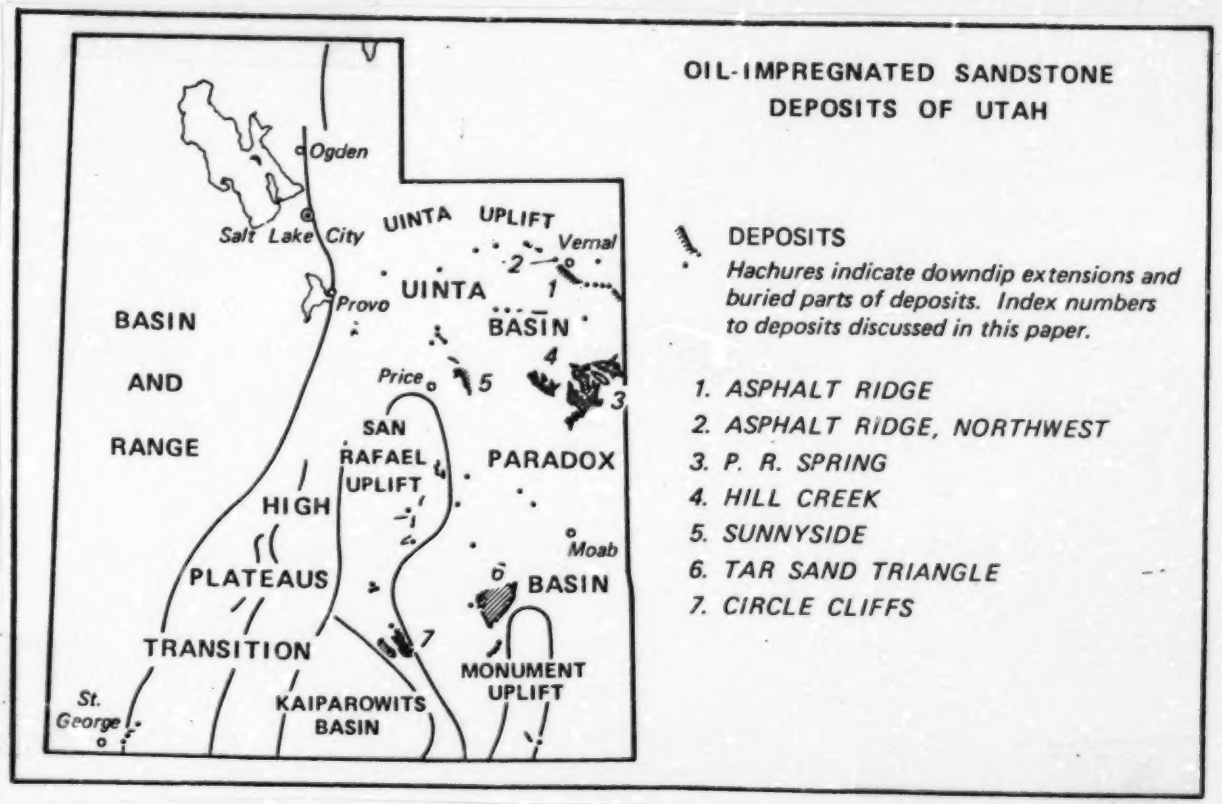

Figure 1. Location map of oil-impregnated rock deposits of Utah. (3)

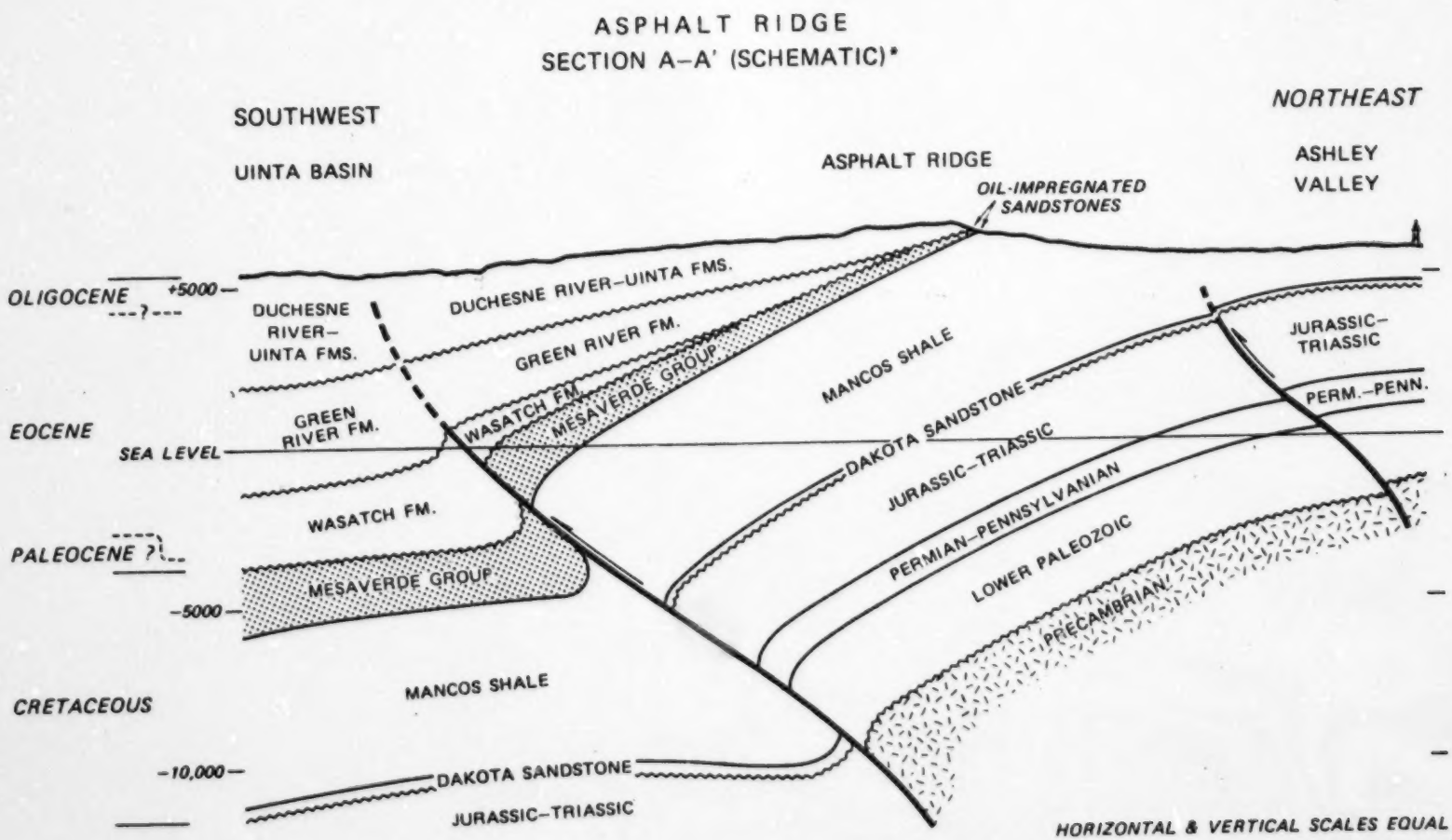

Figure 2. Geological stratigraphy of Asphalt Ridge. (3)

Asphalt Ridge has been described as a cuesta which runs in a northwest direction for approximately 15 miles. The tar sands deposit extends 12 miles along the strike of the ridge in two sections separated by an "angular nonconformity" (see Figure 3).(3) These units are comprised of the Mesaverde group (late Cretaceous), the Uinta and the Duchesne River formations (Eocene-Oligocene). Within the Mesaverde grouping two formations of marine origin occur; namely, the Asphalt Ridge and Rim Rock sandstone. The Rim Rock sandstone formation which exhibits the greatest exposed thickness of oil impregnation ranges from less than 100 to over 300 feet in thickness. The Duchesne River Formation (Eocene) of continental origin overlays these strata with material consisting of conglomerate, sandstone, siltstone and shale.

It is difficult to determine the exact size of the tar sands deposits to be found at Asphalt Ridge since very little subsurface data is available. However, assuming that the oil impregnation observed at the surface extends continuously into the subsurface behind the outcrop, an estimate of approximately 1.05 billion barrels has been given (see Table 1 below).(3)

TABLE 1. MEASUREMENT OF ASPHALT RIDGE TAR SANDS DEPOSITS

Stratigraphic Unit - Duchesne River Formation Rimrock Sandstone	
Oil in place (millions of barrels)	
Estimated	1,048
Measured	873
Areal extent (miles^2)	20-25
No. of principal pay zones	2-5
Gross thickness (range in feet)	0-500

Characterization

The general composition of Uinta Basin tar sands deposits may be divided into several categories: bitumen content; water content; porosity and air permeability (see Table 2). Since bitumen saturation is an important factor in extracting petroleum from tar sands, lower limits for viable mining operations have been established. Bitumen content should not be less than 10 (% wt.) for most mining processes with in-situ processes requiring slightly less. Small fines content, low water percentage and high permeability of Asphalt Ridge tar sands make it suitable for bitumen recovery via in-situ processes.(1)

TABLE 2. TYPICAL TAR SANDS COMPOSITION (UINTA BASIN-P.R. SPRING) (1)

Minerals	Weight Percent
Sand (44 microns)	90.5
Fines (44 microns)	1.5
Bitumen	7.5
Water	0.5
	100.0
Porosity (vol. %)	8.4
Air permeability (millidarcies)	133

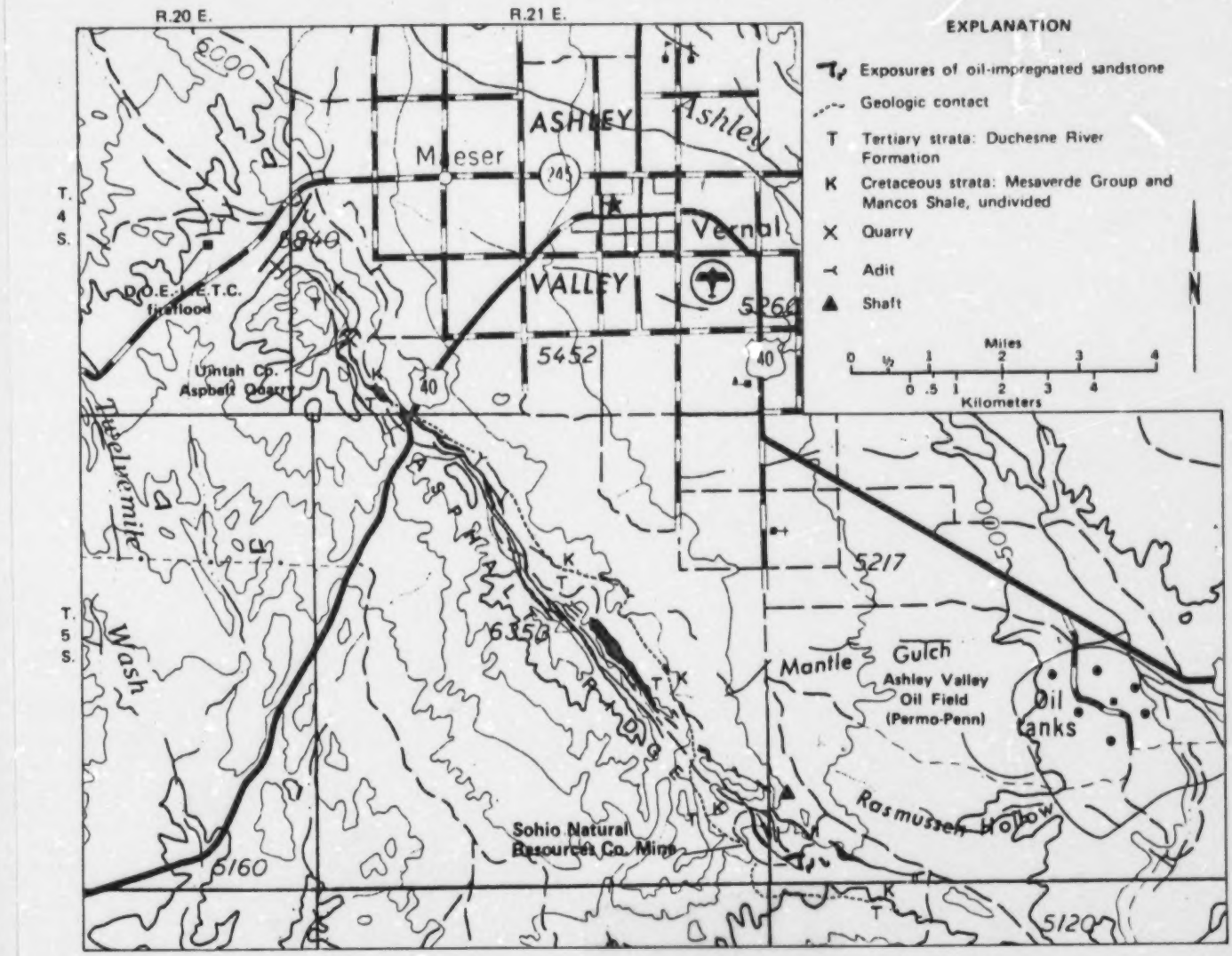

Figure 3. General geology and oil-impregnated sandstones of Asphalt Ridge and Asphalt Ridge Northwwest, Northeastern Uinta Basin, Utah. (3)

Physical property data and elemental analyses for representative Asphalt Ridge tar sands bitumen were provided by researchers at the Department of Energy's (DOE) Laramie Energy Technology Center (LETC)(1). The data is presented in Table 3 below.

TABLE 3. PHYSICAL PROPERTY ANALYSIS OF ASPHALT RIDGE TAR SANDS BITUMENS (1)

Bitumen	
Specific gravity	.970
API	14.4
Atomic C/H	.606
Molecular weight (Ave.)	668
Viscosity (centipoises, 77°F)	2,950,000
Asphaltenes (wt. %)	3.4
Elemental Analysis (wt.%)	
Carbon	85.3
Hydrogen	11.7
Nitrogen	1.0
Sulfur	0.14
Oxygen	1.1
Gross Composition (fraction)	
Acid	10.1
Bases	12.9
Neutral Lewis Bases	19.3
Saturated hydrocarbons	29.3
Aromatic hydrocarbons	28.4

Upon analysis of bitumen properties, it may be noted that API gravities correlate favorably with values associated with petroleum residues. A low carbon-tohydrogen ratio indicates that Asphalt Ridge bitumens are less aromatic than other bitumens (e.g., Athabasca) hence, enhancing bitumen processing characteristics. Asphaltene content is a measure of the coke-forming tendency basic to bitumen processing. The high viscosity figure supports the conclusion that elevated temperatures are necessary to cause bitumens to flow properly. Asphalt Ridge bitumens seem to exhibit a relatively low sulfur content which is an important factor in selecting upgrading sequences for bitumen processing as well as waste disposal and discharge practices.

Gross bitumen compositions are also presented in Table 3. All figures were normalized to account for 100% of the bitumen. Functional groups have been partitioned into several groupings: acids (phenols, carbazoles, and carboxylic acids), bases (sulfoxides, amides, pyridine and benzologs) and neutral Lewis bases (ketones and carbazoles).

Recovery of Bitumen

Various methods have been employed to recover bitumen from tar sands. One approach utilizes extraction techniques to recover bitumen from the mined ore. These processes either use water, solvent (diluent) or a mixture of water and solvent. The water is used to separate the bitumen from the ore and as a flotation media. Several hot-water-solvent recovery systems have been tested in recent years. For an example, Arizona Fuels Corporation of Salt Lake City, Utah demonstrated a recovery unit which successfully separated bitumen from the tar sands ore in an above ground retorting facility.(2) The separation is effected by pre-conditioning the tar sands ore in a heated diluent. Then, after the ore decomposes in the hot diluent, it is pumped as a slurry into a flotation chamber. There it is washed several times with an "aqueous solution." The diluent/tar mixture is skimmed from the flotation chamber and conveyed to an oil recovery unit where the sludge and water are removed as waste byproducts. The diluent/tar mixture is separated via distillation with the diluent returned to the process and the oil collected for marketing.(2)

Similar processes have been tested in pilot facilities sponsored by the State of Utah and/or the University of Utah Research Institute. One of two samples used in this study came from a pilot facility engaged in experimental work utilizing hot water solvent extraction techniques. The pilot facility was operated jointly by the State of Utah and a privately owned company, Enercor.

It has been recognized that a large percentage of tar sand deposits are embedded too deeply to be mined economically. Therefore, the oil must be recovered in-situ. Most in-situ methods involve means for reducing viscosity as well as supplying energy for displacement of the bitumen. For direct combustion techniques, two wells are drilled through the overburden layers into the tar sands deposit area. Ignition occurs at the air injection well inducing a combustion front to move through the formation in the direction of air flow toward the production well. During combustion, part of the bitumen is thermally cracked providing fuel for the duration of combustion. Oil and water vapors are generated as a result of the combustion sequence where they move forward into the unheated portion of the deposit area called a reservoir. Here, the vapors cool and condense.(5) The freed bitumen is then pumped to the surface. Core sections were obtained for this study from a direct combustion in-situ experiment conducted at Asphalt Ridge, Utah, by the LETC.

Whether the tar sands are retorted and discarded above ground following a surface or underground extraction process or combusted in-situ, environmental problems exist which necessitate leachate characterization studies on both naturally occurring and processed tar sands matrices.

SECTION 2

RESEARCH PROTOCOL

Experimental Program

In order to determine the chemical composition of tar sands leachate approximately twenty-eight feet of three inch tar sands core was obtained from the TS-2C direct combustion in-situ experiment conducted at Asphalt Ridge by the LETC. Segments of the core were recognized as being either combusted or non-combusted. Of the total length of core received by the researchers, only ten feet was identified as being affected by combustion. The combusted section contained no visible bitumen content; whereas, the non-combusted section contained an abundant amount. In addition, a fifty-five gallon drum of processed tar sand (spent sand) was obtained from Enercor's above ground retort pilot plant in Salt Lake City. All together three types of tar sands matrices were to be extracted and analyzed: combusted core (cc), uncombusted core (uc), and spent sand (ss).

Shake and extraction tests were conducted in an effort to assess the characteristics of tar sands leachate. The leachate was analyzed by the EPA analytical support group IERL, Cincinnati, for parameters specified by the drinking water quality criteria (6) and for toxic components thought to be present in the leachate. In all, twelve different water quality tests plus trace element analyses were conducted on the leachate samples generated from the shake and extraction procedures (see Table 4).

Materials & Methods

Tar Sand Cores - In July of 1981, the Oil Shale and Energy Mining Branch, IERL, received the three inch diameter core from LETC. There were several different core lengths. The Army Corps of Engineers, Ohio River Division Laboratory, was contacted to crush portions of the core. In accordance with specifications required by the extraction procedures, the material was screened through a 9.523 mm sieve (3/8" U.S. standard sieve opening). Although the specifications were met for the combusted portion of the core, the uncombusted core gummed-up in the mechanical crushers used by the Corps. An alternate method of crushing the material with a press proved to be more successful.

The spent sand from the above-ground retort operation was kept in a covered drum to avoid contamination. Samples were taken from the drum as needed. The sand was dark brown in color and imparted a heavy petroleum odor. A sieve analysis was performed on the spent sand (see Figure 4).

Extraction Procedure (EP) Toxicity Test (7)

The Resource Conservation and Recovery Act's (RCRA) EP Toxicity Test is a laboratory test designed to simulate the leaching that a waste will undergo

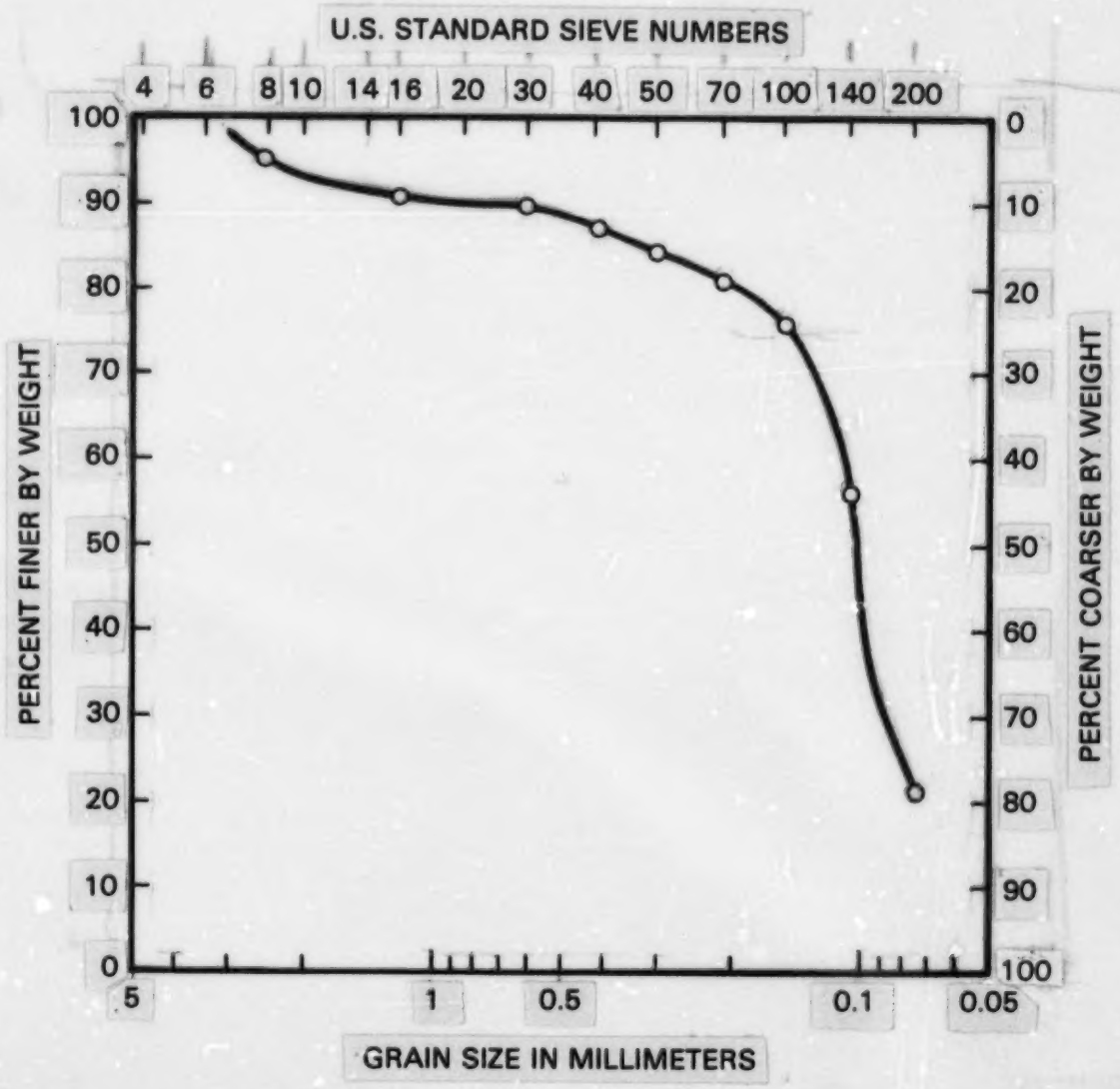
U.S. STANDARD SIEVE NUMBERS
4 6 8 10 14 16 20 30 40 50 70 100 140 200
100 90 80 70 60 50 40 30 20 10 0
PERCENT FINER BY WEIGHT
0 10 20 30 40 50 60 70 80 90 100
PERCENT COARSER BY WEIGHT
5 1 0.5 0.1 0.05
GRAIN SIZE IN MILLIMETERS

FIGURE 4. Sieve Analysis of Spent Tar Sand.

when disposed in a landfill. A representative sample of the waste is extracted at pH 5 with distilled water and acetic acid. The extract is then analyzed for various substances. A rotary extractor was used to conduct all extraction procedures. The methods for leaching the tar sands are outlined below.

1) Extraction of solid material - Two 100g samples of the spent surface, processed tar sands, two 100g samples of the crushed, affected core, and two 100g samples of the crushed unaffected core (six samples total) were weighed and placed in individual cells in an extractor with sixteen times their weights (1.6 liters) of deionized water. An acceptable extractor is one which imparts sufficient agitation to the mixture to not only prevent stratification of the sample and extraction fluid, but also to insure continuous contact. A six-bottle rotary extractor obtained from the Associated Design Manufacturing Co. was utilized.

   The pH was maintained manually with a calibrated pH meter. The extractor was turned on for one minute, then stopped. The pH was adjusted to 5.0 + 0.2 with 0.5 N acetic acid and then the extraction continued for 24 hours. The pH of the solution was adjusted at 15, 30, and 60 minute intervals, moving to the next longer interval if the pH did not have to be adjusted more than 0.5 pH units. The adjustment procedure was continued for the first six hours. If at the end of the 24 hour extraction period, the pH of the solution was not below 5.2 and a maximum amount of acid (4 g per gram of solids) had not been added, the pH was adjusted to 5.0 + 0.2 with the extraction continuing for an additional four hours. Again the pH was adjusted at one hour intervals.

2) Separation Procedure - A vacuum filter employing coarse to fine filter media was used to separate the liquid phase from the solid. The liquid was stored at 4°C, unless otherwise specified, for subsequent analysis.

3) Procedure for Analyzing Extract - Lab analyses consisted of the list shown in Table 4. The stored liquid from step 2 was segregated into separate flasks and preserved as required. The individual liquid samples were prepared for analysis and analyzed within the specified holding times.

   This procedure was run in triplicate and is consistent with the other extraction methods (see below). A modified EP toxicity test was also performed on samples without the addition of the acetic acid. The same separation and analysis procedures were followed.

ASTM (D-3987) Method A-1 Modification (8) - The ASTM shake extraction test is a standard test intended to be used as a rapid means for obtaining an extract from solid waste. The extract is then examined for the release of various constituents. This method provided a third set of leachate data, offering a more complete environmental assessment.

The procedure for this test utilizing the extractor described above follows the steps listed below.

TABLE 4. LABORATORY ANALYSES FOR TAR SAND SAMPLES

Measurement	EPA Method	Sample Volume	Holding Time	Container***	Preservation
1. pH	150.1	--	2 hr.	P,G	Determine on site
2. Temperature	170.1	--	--	P,G	Determine on site
3. Chloride	Ion chromatograph**	200ml	7 d.	P,G	None
4. Alkalinity (on water-only Bicarbonate, carbonate	Titration 310.1	200ml	14 d.	P,G	4°C
5. Cyanide, total	Ion chromatograph**	50ml	14 d.	P,G	4°c
6. Ammonia	Electrode 350.3	150ml	28 d.	P,G	4°C pH<2 (H_2SO_4)
7. Fluoride	Electrode 340.2	50ml	28 d.	P	None
8. Mercury: Dissolved	AAS - cold vapor 245.1	400ml	28 d.	G	Filter pH< (HNO_3)
9. Sulfate	Ion chromatograph**	300ml	28 d.	P,G,	4°C
10. Sulfide	Titration 376.1	500ml	28 d.	P,G	4°C Zinc Acetate
11. Conductivity Filterable	120.1	100ml	28 d.	P,G	4°C
12. Carbon Total Organic	415.1	20ml	28 d.	G	pH< (H_2SO_4)
13. Residue Total Suspended	160.0	500ml	--	G	None
14. Metals*: Dissolved	AAS	500ml	6 mo.	P,G	pH< (HNO_3)

*Metals: Al, As, Ba, Ca, Fe, Ni, K, Na, Zn.
**Not an EPA method.
***p = plastic, g = glass

1) Place 70 grams of sample in the leach container, then add 1400 ml of the test water.

2) Close the container and shake to uniformly mix the contents.

3) Place the container on the extractor so that the top of the container is four (4) inches above the holder and the bottom of the container is four (4) inches below the holder (center mounted). Use the remaining 100 ml of water to wash down the sides of the container.

4) Turn on the extractor and agitate the sample for 18 hours.

5) Separation and analysis procedures - follow same procedure used for RCRA EP toxicity tests.

Chemical Analysis

During the course of the six week study, the three tar sands matrices were extracted by using EP toxicity (with and without acidification) and ASTM tests. Three runs were conducted successively. All sample sets were analyzed by the Analytical Support Group, Program Operations Office, IERL-Ci. The laboratory used EPA approved methods (10) and Standard Methods, 15th ed., (11) when performing leachate (extract) analysis. Trace metal (inorganics) analysis was accomplished with a Perkin-Elmer 4000 atomic absorption spectrophotometer with an accessory HGA 400 graphite furnace when necessary (e.g., arsenic).

Precision and Accuracy (QA/QC)

Quality control procedures were used for the determination of various constituents so that the precision and accuracy of the analytical techniques could be properly documented. Accuracy of the data generated during this study was evaluated by calculating recovery efficiency for samples spiked in the laboratory with known concentrations of analytes. This was determined by computing the percent recovery (%R) of a known sample concentration spiked with a prepared standard. These standards were either prepared in the analytical laboratory performing the analysis or obtained from the Environmental Monitoring Support Laboratory (EMSL), EPA. Percent recoveries were computed by dividing the amount recovered by the amount added. An aliquot of 1 ml sample included a QA spike for recovery determinations. Percent recovery is a measure of accuracy where recoveries of 100 + 10% are deemed acceptable with 100 +5% being optimum. Analysis of total suspended solids (TSS) offers the only exception to this rule. Percent recoveries in the range of 100 + 20% are acceptable when considering the hygroscopic nature of TSS. QA spikes are indicated in the data tables respective to those sample sets spiked for recoveries.

Quality control (QC) samples were also utilized with the accuracy of testing procedures being based upon the difference between measured values and actual values. These QC values are also reported as percent recovery (%R). The QC standards were either prepared from Standard Methods in the lab or obtained from EMSL. QC values are presented in the data tables respective to the set of samples with which they were to be analyzed.

SECTION 3

RESULTS

The data for total suspended solids, total organic carbon and alkalinity are also presented in graphic form in Figures 5, 6, 7, and 8, respectively. The data generated from the extract analyses are presented in Tables 5 through 13. When QA and QC results were obtained, they were presented in association with the sample set to which they correspond. Each data block represents results pertaining to a particular extraction method. Some analyses were not performed on the samples from the ASTM extraction procedure, since results from the EP toxicity tests indicated that the analyte concentrations would be too close to the detection limit to provide meaningful data. Therefore, there are no ASTM results for chlorides, fluorides, sulfides and cyanide.

The results of the pH adjustments for EP toxicity procedures utilizing the acid adjustment indicated that the combusted and uncombusted cores were on the basic side of the pH spectrum. All of the allotted amount of acetic acid (40 ml) was added to the samples to keep the pH under 5 ± 0.2. In most instances the full complement of acid was also administered to adjust pH for the spent sand samples.

Blanks were run for most of the determinations and their associative values are presented below their respective data blocks. These blanks were derived from the "clean" sand that was extracted simulatenously and similarly for each of the three extraction procedures. With the exception of total organic carbon (TOC) all other determinations focused on inorganic chemical parameters.

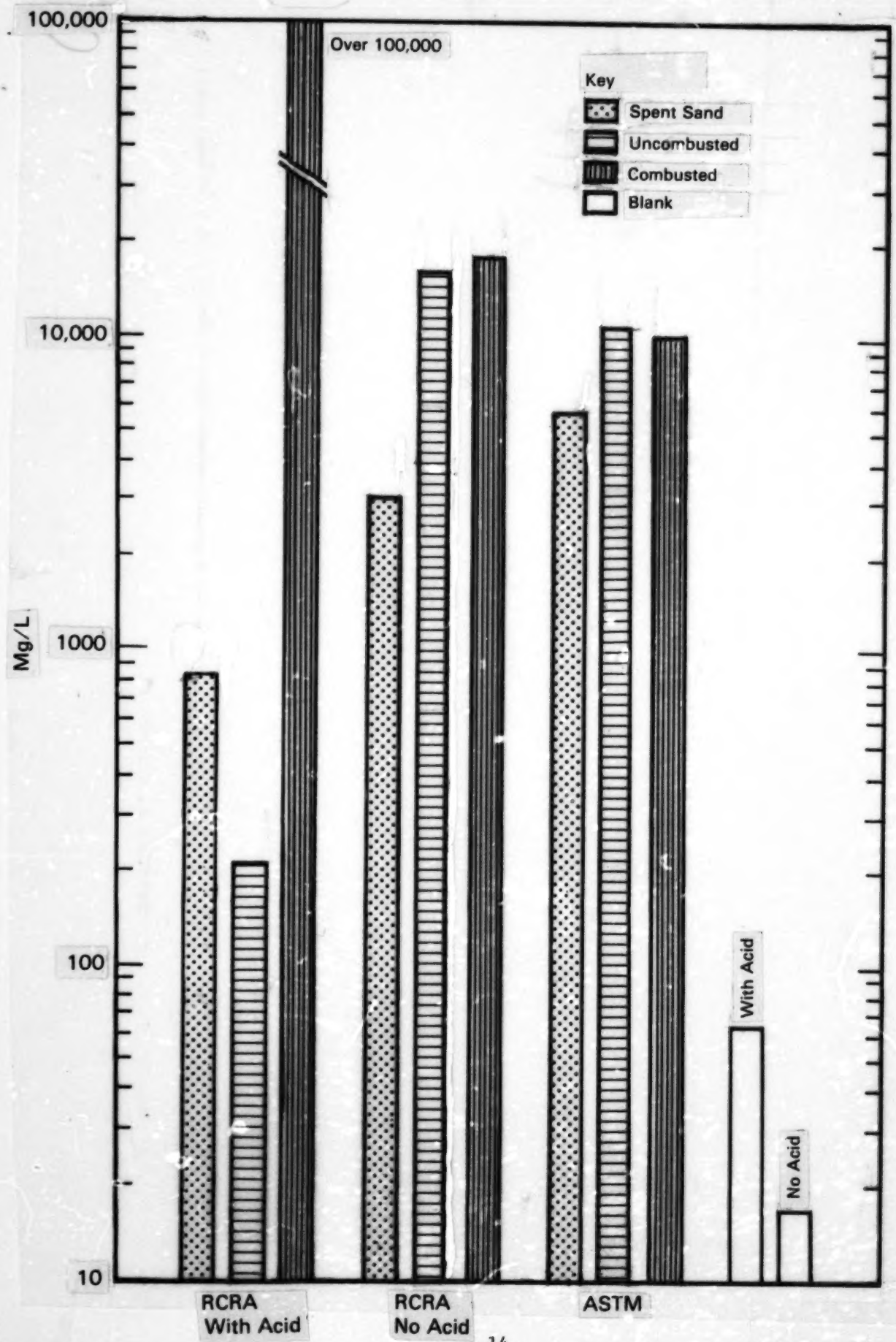

Figure 5. Total Suspended Solids.

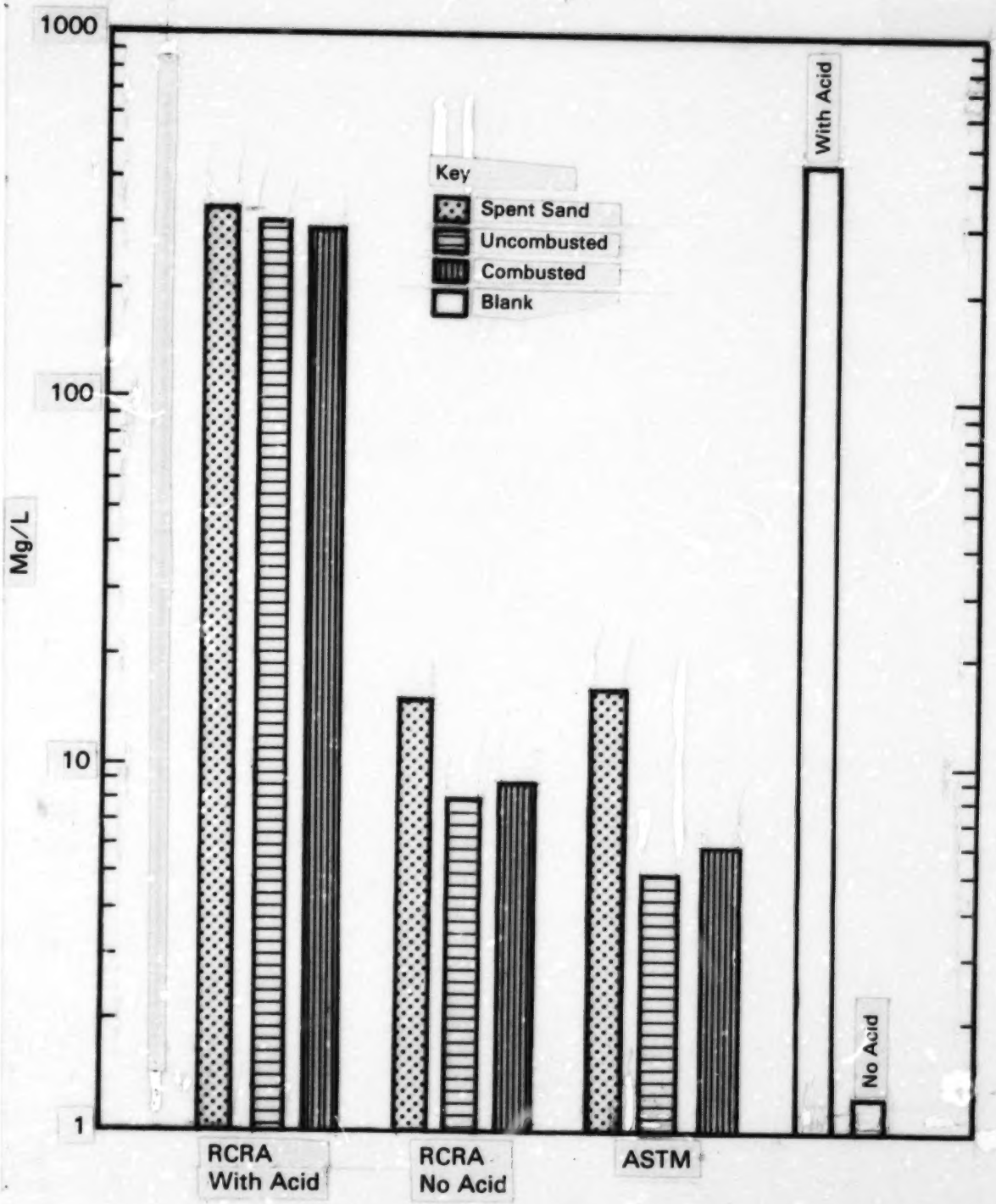

FIGURE 6. Total Organic Carbon.

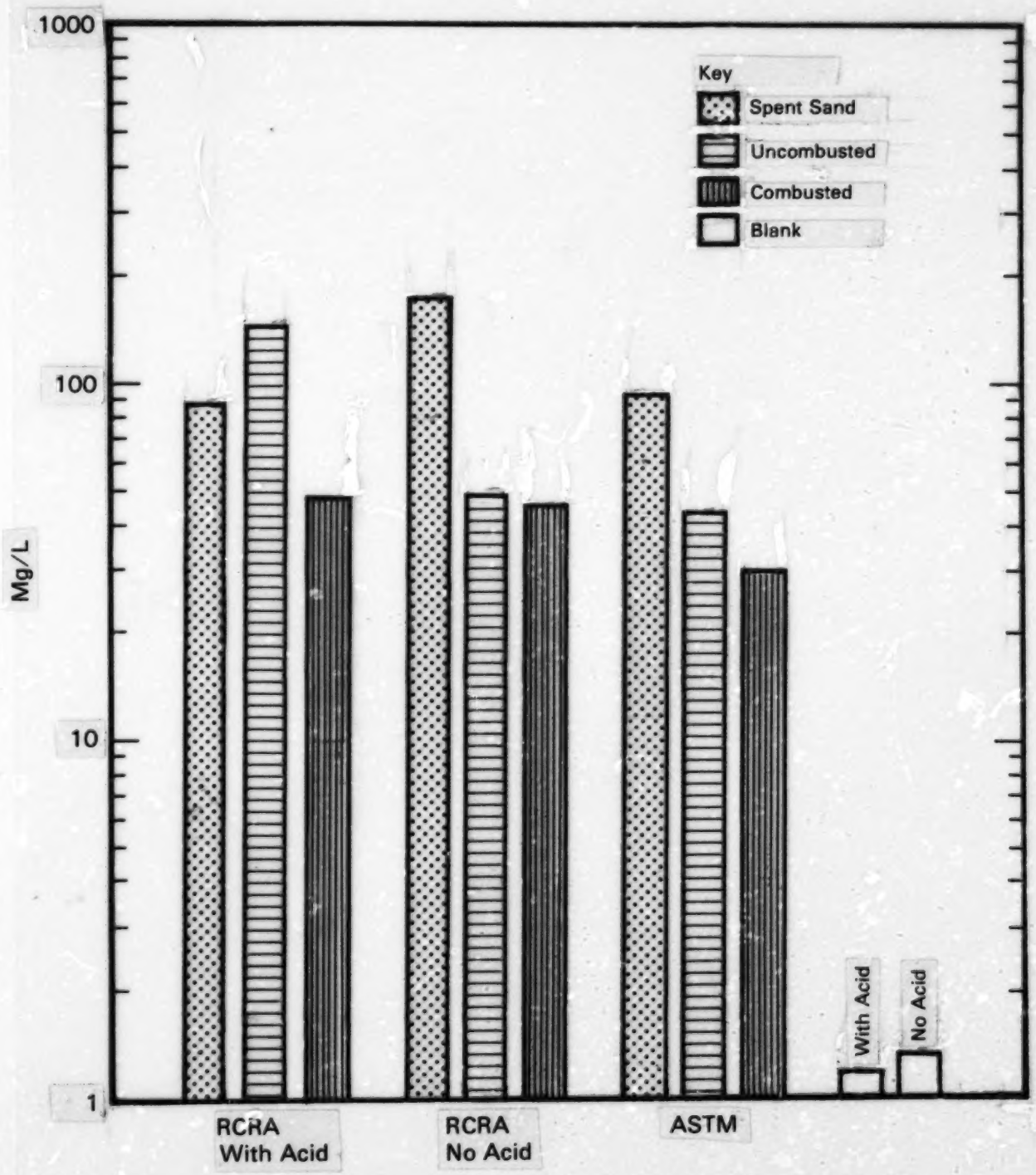

FIGURE 7. Sulfate.

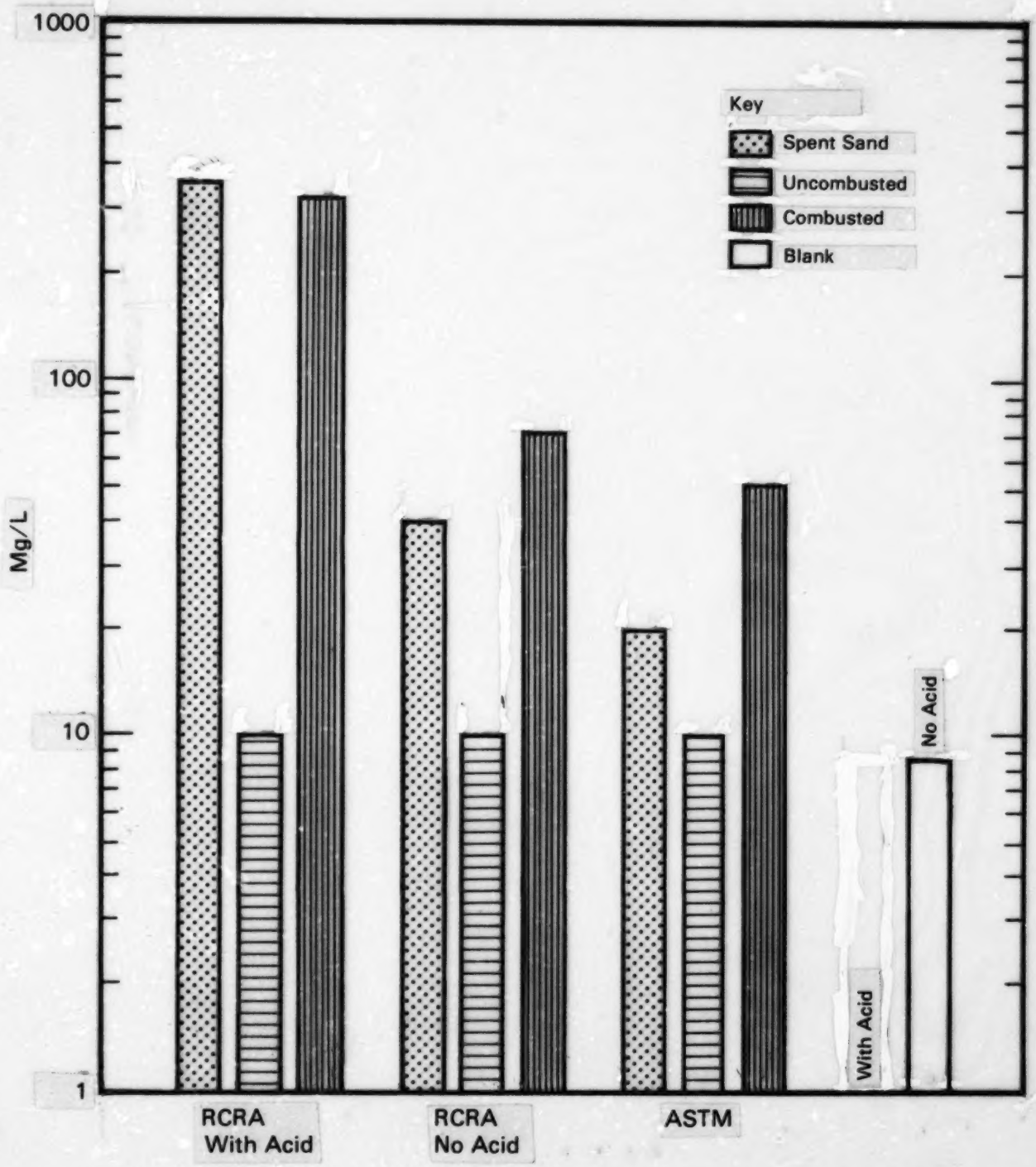

FIGURE 8. Alkalinity as $CaCO_3$.

Summary of Analytical Results

TABLE 5. SULFATES (EPA METHOD #375.4, ION-CHROMATOGRAPH)

EP Toxicity With Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	114	99	228		105	
2	53.4		47.5		13.2	98
3	109		41		18	100

Blank = 0.89 mg/l

EP Toxicity Without Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	101	90	47	86	38	84
2	124		59		50	
3	119	99	45		30	99

Blank = 1.39 mg/l

ASTM
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	74	104	34	114	31	114
2	112	97	57	97	33	103
3	92	100				

Fifteen out of 25 samples were spiked to monitor recovery efficiency (QA) with recoveries ranging from 84 to 114%. The average recovery was 92%.

TABLE 6. CHLORIDES (EPA METHOD #325.3 WITH ELECTRODE)

EP Toxicity With Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	1.5		1.6	107	1.6	
2	1.3		1.1	104	1.3	
3	1.4	101	1.05	97	1.2	98

Blank = 0.99 mg/l

EP Toxicity Without Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	0.9	124	0.57	103	1.56	89
2	1.18	97	0.73	104	1.9	80
3	1.11	101	0.74		0.8	101

Blank = 0.47 mg/l

All values are averages of duplicate analytical determinations with the exception of QA recovery efficiencies.

TABLE 7. FLUORIDES (EPA METHOD #340.2)

EP Toxicity With Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	0.4		1.4		<0.1	
2	0.12		<0.1		0.1	
3	0.15		<0.1		0.1	

Blank = 0.0 mg/l

EP Toxicity Without Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	.24	115	.16		1.3	
2	.18	88	.16	100	1.09	
3	.2		.15		1.27	

Blank = 0.0 mg/l

Duplicates were run on all samples and the results were averaged. Three QA samples were performed with recovery efficiencies ranging from 88 to 115%.

TABLE 8. SULFIDES (EPA METHOD #376.1 - TITRATION)

EP Toxicity With Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	-		-		-	
2	.3		.4		.4	
3	.3		.3		.6	

EP Toxicity Without Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	.9		<.1		.6	
2	.2		.2		.8	
3	.4		.2		1.0	

The values recorded for the sulfide determination were too close to the detection limit to warrant QA spikes.

TABLE 9. ALKALINITY AS $CaCO_3$ (EPA METHOD #310.1 - TITRATION)

EP Toxicity With Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	17		8.1		115.5	
2	507		0		446	86*
3	577		0		510	

*EMSL Standard Addition
Blank = 0 mg/l

EP Toxicity Without Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	39.1		9.7		60.0	
2	47.2		7.7		76.6	
3	42.2	99.5	7.2	97.6	60.0	95

Blank = 8.1 mg/l

ASTM
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	31.0		12.4		55.1	
2	35.2		6.2		51.1	
3	25.3		-		-	

Two QC primary standards were prepared by EMSL for analysis. The results are as follows:

QC Sample	Reported Value	True Value	%R
WP 478	22.56 mg/l	21.7 mg/l	104%
WP 478 (2.25)	53.82 mg/l	54.3 mg/l	99%

TABLE 10. CONDUCTIVITY (EPA METHOD #120.1 - WHEATSTONE BRIDGE)

EP Toxicity With Acid
Tar Sands Matrix

Run No.	SS umhos/cm	UC umhos/cm	CC umhos/cm	QC %R
1	1300	1000	1000	99
2	1500	300	1000	99*
3	1300	1300	400	99

EP Toxicity Without Acid
Tar Sands Matrix

Run No.	SS umhos/cm	UC umhos/cm	CC umhos/cm	QC %R
1	270	130	160	96.2
2	330	150	190	99
3	280	130	180	99

ASTM
Tar Sands Matrix

Run No.	SS umhos/cm	UC umhos/cm	CC umhos/cm	QC %R
1	220	120	170	93
2	280	150	100	94
3	220	-	-	99

*A 0.01m KCL standard was prepared in the laboratory in accordance to Standard Methods and evaluated for recovery efficiency (% R). Specific conductance measurements are used in water analysis to obtain a rapid estimate of the dissolved solids content of a sample. Significantly higher values (umhos/cm) were recorded for the EP toxicity procedure using acid adjustment.

TABLE 11. TOTAL SUSPENDED SOLIDS (EPA METHOD #160.0)

EP Toxicity With Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	1,340		320		638	
2	810		348		446	
3	264		28		205,150	

Blank = 63 mg/l QA 133%R

EP Toxicity Without Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	6,640		626	83	31,632	
2	4,220		4,596		7,456	104
3	1,968		2,894	89	17,216	

Blank = 26 mg/l QA 127%R

ASTM
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R
1	7,420		19,332		63,932	
2	5,094	37	3,720		15,500	
3	6,995	94	-		-	

The QA spike for TSS determination came from EMSL and was prepared from a primary standard.

TABLE 12. TOTAL ORGANIC CARBON ANALYSIS (EPA METHOD #415.1)

EP Toxicity With Acid
Tar Sands Matrix

Run No.	SS mg/l	QA %R	UC mg/l	QA %R	CC mg/l	QA %R	QC %R
1	299		270		230		98
2	332		309		299		97
3	335	103	347	106	320	105	101

Blank = 1.1 mg/l

EP Toxicity Without Acid
Tar Sands Matrix

Run No.	SS mg/l	UC mg/l	CC mg/l	QC %R
1	15	8	5	99
2	13	9	9	98
3	15	6	12	

Blank = 0.91 mg/l

ASTM
Tar Sands Matrix

Run No.	SS mg/l	UC mg/l	CC mg/l	QC %R
1	14	6	12	98
2	13	6	12	
3	14			

QC samples were obtained from EMSL with recovery efficiencies ranging from 97 to 101%. Very little TOC was present in the unacidified extraction methods.

The extracts were analyzed for cyanide by an electrode method (not an approved EPA method). However, results were recorded below the detection limit (<0.05 mg/l) for both EP toxicity procedures.

Trace Metal Analysis (AAS)

The following table shows the averages of the trace metal concentration measurements for the three runs conducted. The combusted core showed significantly higher concentrations of trace metals. Calcium, magnesium, potassium, and sodium were present in the highest concentrations. Arsenic, barium, mercury, nickel and zinc were below the detection limit.

TABLE 13. TRACE METAL ANALYSIS (mg/l)

	EP Toxicity with Acid			EP Toxicity no Acid			ASTM			QC
	CC	UC	SS	CC	UC	SS	CC	UC	SS	%R
Al	.1	2.3	.3	8.3	.16	2.4	19.9	.15	.23	109
Ca	176	32	378	78	17	65	36	18	47.6	102
Fe	.5	3.0	.83	7	.5	1.5	2.9	.6	.57	100
Mg	61.6	3.4	12.9	31.4	2.7	5.0	13.5	2.9	2.5	98
K	9.0	1.4	1.9	9.4	1.3	1.7	8.7	1.6	4.0	105
Na	5.6	2.9	2.3	6.4	3.8	3.2	9.2	1.5	2.1	104
ZN	.04	.32	.08	.22	.03	.03	7.3	.04	.18	100
Ba	---------- All less than 1.0 ----------									98
Hg*	---------- All less than .001 ----------									-
Ni	---------- All less than .2 ----------									100
AS	---------- All less than .02 ----------									108

*All tar sand samples were analyzed in duplicate for mercury (Hg) and seven of them were spiked with 1 ppb Hg. Recoveries could not be computed for the spikes because the concentration of the unspiked samples were above the blank but too low for meaningful detection.

SECTION 4

DISCUSSION

Based on the conventional water quality determinations examined during this study, both shake and extraction procedures provided some insight into the fate of various contaminants that may be prevalent in the leaching of tar sands residue and processed waste. Since the primary objective in this study was to charactize the constituents present in the leachate, no attempt was made to model contaminant migration into groundwater reservoirs and streams.

A preliminary comparison can be made among the various extraction methods especially with respect to the acid addition step present in the RCRA EP toxicity test. When the EP toxicity test was run with the acetic acid adjustment, more often than not, higher concentrations were recorded. This is to be expected since many trace metals will tend to be more leachable under acidic conditions. However, it is important to evaluate the same parameters for neutral and/or basic conditions, since this type of information may more closely represent field disposal conditions. Unless otherwise stated, most of the discussion will revolve around results obtained from the RCRA EP toxicity procedure (using acid) since it is the most sensitive of the three methods performed.

In examining the data for hazardous waste contaminants, only three (arsenic, barium, and mercury) are listed in the Federal Drinking Water Quality Standards.(11) These values are only provided as a reference point; rather than to imply this discharge should meet drinking water standards. Those contaminants included in the standards which were measured in this study are presented in Table 14 below.

TABLE 14. WATER QUALITY STANDARDS* (11)

EPA Hazardous Waste Number	Contaminant	Maximum Concentration (mg/l)	Measured Concentration (mg/l)
D004	Arsenic	.05	< .02
D005	Barium	1.0	<1.0
D009	Mercury	.002	< .001

*Established by the National Interim Primary Drinking Water Regulations.

Upon examination of the results, it is apparent that none of the hazardous constituents listed in Table 14 are in excess of the maximum allowable concentrations.

Another approach to examining the potential for groundwater contamination is to compare the results of the extraction tests to water quality criteria which have been summarized by the Environmental Criteria and Assessment Office (ECAO), EPA.(6) Of particular interest are the priority pollutants prevalent in the sample extractions. The following table lists some values established by that office for those contaminants found in the tar sands leachate.

TABLE 15. WATER QUALITY CRITERIA FOR PRIORITY POLLUTANTS[a] (12)

Criteria Priority Pollutant	Average Daily Intakes[b] ADI (mg/l)	Uncertainty Factor
As		
Hg	.01	10
Ni	.75	1,000
Zn	7.5	10
Cyanide	3.8	100

[a]Federal Register 45:79347, 1980
[b]Average Daily Intakes (ADI) are based upon the water consumption of 2 L/day tainted by the presence of the pollutant

Upon reviewing Tables 13 and 15, it is apparent that, with concentrations of cyanide less than the detectable limit of .05 mg/l, very little opportunity exists for cyanide to be a problematic constituent in tar sands leachates. The other listed priority pollutants, zinc, mercury and nickel are present in very low concentrations. All the other trace metals not listed as priority pollutants yielded relatively low concentrations for tar sands leachate.

With respect to other parameters analyzed in this study, only TOC and sulfate determinations exhibited concentrations high enough to cause any concern. Whether this level of concentration can be expected from the addition of acid for pH adjustment during the extraction procedure or whether organic constituents are released, is a matter that deserved more consideration. A more thorough characterization in the future may be necessary to look at specific organic analyses; especially, phenols and compounds associated with the various functional groups prevalent in tar sands bitumen.

SECTION 5

CONCLUSIONS

The initial laboratory tests conducted under this study indicate that leachates from spent tar sands may not contain significant amounts of toxic pollutants but may contain substantial amounts of sulfate and total organic carbon (TOC). Only five constituents of the specific parameters analyzed were identified as priority pollutants (e.g., those elements posing the greatest risk to health and the environment). Of the five priority pollutants tested (cyanide, mercury, nickel, arsenic and zinc), all exhibited low concentrations. However, concentrations of sulfate and TOC were fairly high and could impact surface and/or groundwater quality. Those trace elements which were present to any significant degree were not considered to be highly toxic or deleterious to the environment.

It is recommended that further work be undertaken to characterize specif--ic organics, such as, hydrocarbon combustion products and phenols. It has been recommended that digestion tests be performed on the spent filter paper from the shake and extraction tests. Future work may involve some groundwater modeling of the more problematic constituents characterized by this study.

REFERENCES

1. Oblad, A.G., et al., "Recovery of Bitumen from Oil-Impregnated Sandstone Deposits of Utah." In Oil Shale and Tar Sands, ed. John Smith and Mark Atwood, NY, NY: American Institute of Chemical Engineers, 155, 72 (1976): 69-78.

2. Lowe, R.M., "The Asphalt Ridge Tar Sand Deposits," In Oil Shale and Tar Sands, ed. John Smith and Mark Atwood, NY, NY: American Institute of Chemical Engineers, 155, 72 (1976): 55-60.

3. Campbell, J.A. and Ritzma, H.R., "Geology and Petroleum Resources of the Major Oil-Impregnated Sandstone Deposits of Utah." In The 10CC Monograph Series: Tar Sands, ed. Douglas Ball, et al., Interstate Oil Compact Commission, Oklahoma City, Oklahoma, (1982): 27-43.

4. Kuuskraa, V.A. and Doscher, T.M., "The Economic Potential of Domestic Tar Sands." In The 10CC Monograph Series: Tar Sands, Ed. Douglas Ball, et al., Interstate Oil Compact Commission, Oklahoma City, Oklahoma, (1982): 185.

5. Cupps, C.Q., at al., "Field Experiment of In-situ Oil Recovery from a Utah Tar Sand by Reverse Combustion." In Oil Shale and Tar Sands, ed. John Smith and Mark Atwood, NY, NY: American Institute of Chemical Engineers, 155, 72, (1976): 62, 63.

6. U.S. EPA, "Summary of Published Acceptable Daily Intakes (ADIS) for EPA's Priority Pollutants." Environmental Criteria and Assessment Office, U.S. EPA, Cincinnati, Ohio, (1983).

7. U.S. EPA, "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods." (SW-846B), U.S. EPA, Washington, DC, (1981).

8. ASTM, "Standard Test Method for Shake Extraction of Solid Waste with Water." (D-3987), In Annual Book of ASTM Standards, ASTM, Philadelphia, Pennsylvania, (1981): 2652.

9. U.S. EPA, "Methods for Chemical Analysis of Water and Wastes." EPA-600/4-79-020, U.S. EPA, Cincinnati, Ohio, (1979).

10. American Public Health Assoc. Standard Methods for the Examination of Water and Wastewater, 15 Ed., APHA, AWWA, AND WPCF, Washington, DC, (1980).

11. 40 CFR Part 141, EPA Water Programs, December 24, 1975 (Vol. 40, No. 248).

12. Federal Register, 45:79347, (1980).